

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

REGION I

J. F. KENNEDY FEDERAL BUILDING, BOSTON, MASSACHUSETTS 02203

February 18, 1986 Dr. Philip Gidley Gidley Laboratories, Inc. Fairhaven, MA 02719 Dear Dr. Gidley: I am forwarding a copy of the Corps	Superfund Records Center SITE: New Prefer & BREAK: 4.07 OTHER: 5010
your comments on the Engineering Fe have any additional questions or coat (617)223-1951 or Norman Francing Experiment Station at (601)634-3703	easibility Study. If you omments, please contact me gues at the Corps' Waterways
Sincerely,	
Jackel Prince	
Jackie Prince	2/26/86
Enclosure	
Dear Joebie Prince: This is our in	itial response to
your leller and the	Laeview the response.
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We are however, items which are ex cer EN-799 of 10/12/74 (.	herewith appending pts from our Report
EN-799 of 10/12/74 (.	now out of print) - see
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sentences	0.8

GIDLEY LABORATORIES, INC. CHEMICAL AND ENVIRONMENTAL SCIENCES FAIRHAVEN, MASS., U.S.A.



The Commonwealth of Massachusells Executive Office of Environmental Affairs 100 Cambridge Street Boston, Massachusetts 02202

February 14, 1977

Dr. Philip T. Gidley Gidley Laboratories Fairhaven, Massachusetts

bear Dr. Gidley:

I would like to thank you for the constant flow of information with which you are providing me. Your recent piece on <u>Bredging</u>, <u>Flyash and Sludge Disposal is most interesting and useful</u>. I appreciate your taking the tope and energy to rend us your comments on these particularly vextag environmental problems.

Enclosed is a copy of the minutes of a meeting between the state and the Corps concerning Brown's Ledge. The Corps has apparently agreed to go wholeheartedly ahead with planning for land disposal.

Thanks again for your correspondence.

Sincerely,

Richard E. Chaisson Constal Review Center

REC:sar

L DGING, FLY-ASH AND SLUDGE DISPC :: THE HUMPTY DUMPTY PROBLEM

Environmental pollutants or toxic materials which are generally common to fly-ash emitted from coal-fired power plants and to dredging spoils from rivers, harbors and estuaries of industrial environs are: lead, zinc, chromium, nickel, copper, cadmium, vanadium, berylium, antimony, selenium and arsenic. Specific constituents of particular dredging sediments and of particular fly-ashes will of course vary both in kind and degree, but lead, zinc, chromium, cadmium, nickel, copper are often found in both these sources and in approximately the same range (parts per million or milligrams per kilogram). Usually vanadium, berylium, antimony, selenium and arsenic will occur more frequently in fly-ash than in dredging and usually lox to look range in the fly-ashes. On the other hand, mercury usually is present in industrial harbor dredging in much higher proportions than in fly-ash (in which it may be totally absent). Also organic hydrocarbon toxicants such as P.C.B., D.D.T., organophosphates, benzene, dyes, oils and solvents are found only in dredging spoils and not in fly-ash.

Sludge from municipal waste water treatment plants, handling industrial plant effluents (directly discharged into sewage lines or combined sewage-storm drain lines), often contains similar toxicants in similar ranges to those toxicants present in dredging spoils and/or fly-ash. Typical sludge metals or toxicants are mercury, cadmium, chromium, copper, nickel, lead, zinc, vanadium and selenium. Also in some sludges are found such organic compounds as P.C.B., D.D.T., anthracenes, phenols, chlorinated ketones, and similar pollutants.

Because of the presence of these enumerated toxicants in significant amounts the safe disposal of these three classes (dredging spoils, fly-ash and sludge) requires comprehensive analyses, appropriate siting, containment, and monitoring to avoid, prevent or minimize damage to the environment (potable water supplies, aquifers, fish habitats, shell-fish areas, food crops and similar vital resource areas). Therefore, because of the similar toxicant properties of these three classes it makes good common sense to combine and dispose of two or more of these classes at the same environmentally secure site wherever possible thus simplifying disposal, engineering and monitoring. As an environmental and engineering bonus the combinations often result in acceptability and beneficial end-uses often not feasible when one class alone must be disposed. For example:

A. DREDGING AND FLY-ASH

Fly-ash acts as a desirable soil amendment, dewatering agent and land-fill conscidation material when <u>mixed with wet dredgings high in organic matter</u>, clay and/or fine silt. Ten percent or more fly-ash is desirable and greatly increases the soil bearing strength and decreases the consolidation time of the combination. Lime is a desirable additive component.

B. SLUDGE AND FLY-ASH

This combination consolidates more quickly; partially deodorizes, especially with lime additions; and allows vegetation and crops (preferably non-root food crops and non-food crops such as grasses, shrubs, trees etc.).

C. DREDGING, SLUDGE AND FLY-ASH

The fly-ash consolidates the two other classes and the sludge assists vegetative planting which is desirable if only for erosion control.

Great quantities of fly-ash are often produced and disposal is a costly, difficult and potentially an environmentally hazardous disposal problem. For example, Montaup Electric alone has produced as much as 300 to 500 tons of fly-ash daily and with future oil shortages likely and nearby coal sources possible -- fly-ash can again become a considerable disposal problem.

The combined disposal of two of these classes of materials therefore affords killing two birds with one stone, or paradoxically more important -- two wrongs make a right! To attempt to identify, isolate, treat and/or salvage the toxic constituents of these 3 classes of wastes is as difficult and as impossible as trying to put Humpty-Dumpty back together again. Neither all the King's horses nor all mankind's chemists are equal to the task.

10/12/74 P. T. GIDLEY

Revised 1/30/77

GIDLEY RESEARCH INSTITUTE
Environmental Chemistry & Technology

Fairhaven, Mass., U.S.A.

FAIRHAVEN, MASS., U.S.A.

EXCERPTS FROM

Fly Ash Disposal in a Limestone Quarry

by Jeffrey R. Peffer^a

ABSTRACT

Approximately 740,000 tons (670,000 metric tons) of eastern bituminous coal fly ash were deposited at the abandoned Zullinger limestone quarry from 1973 to 1980. The quarry extended below the water table and was not lined to isolate the ash from the aquifer. The initial filling involved dumping ash directly into the quarry water. The quarry was situated in folded and fractured limestone with relatively high solution-void permeability. Ground-water quality was monitored at the site for seven years through a network of wells. During the first three years of the filling operation, high levels of sulfate were detected in downgradient ground water. However, this initial pollution diminished sharply in 1976 when the ash filled the volume of the quarry below the water table. Long-term groundwater pollution has apparently not resulted. The lack of any significant long-term impact on ground-water quality is attributed to the low permeability of the ash relative to the surrounding limestone aquifer. Typically alkaline limestone ground water at the site is also attributed with neutralizing the low pH fly ash which was deposited.

INTRODUCTION

A. Related Research

Case histories of ground-water contamination from fly ash disposal sites have been developed by Theis et al. (1978) and Theis and Marley (1979) for a site in Michigan; and Cherkauer (1980) for a site in Wisconsin. Both the Michigan and Wisconsin sites involved fly ash disposal in direct contact with highly permeable, unconsolidated sand aquifers. The fly ash deposited at both sites was acidic (4.5 at the Wisconsin site and 5.5-6.0 at the Michigan site).

Sulfate was the primary pollutant in ground water at the Wisconsin site. However, trace elements were not detected beyond the disposal boundary due to the high alkalinity of the sand aquifer. Cherkauer also noted depressed bicarbonate levels in ground water nearest the fly ash fill, due to the low pH of the fly ash leachate.

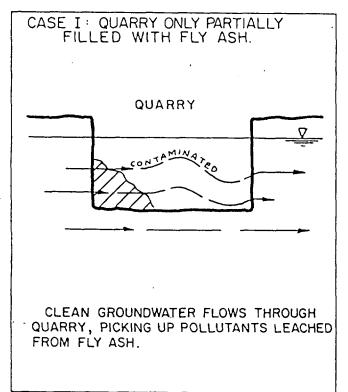
At the Michigan site, sulfate was also found to be the primary pollutant. However, unlike the Wisconsin site, significant levels of trace elements were found in ground water away from the fly ash lagoon boundary. Theis and the other investigators attributed this to the acidity of the fly ash, made no mention of the sand aquifer being alkaline, and recommended lime or limestone addition to the fly ash to raise the pH and immobilize the trace metals.

B. Purpose and Scope

This paper presents the case history of the completed Zullinger quarry fly ash disposal site. The Zullinger quarry is situated in south-central Pennsylvania in folded limestone of the Great Valley, and is typical of many limestone quarries in the northeastern United States. From 1973 to 1980, the abandoned Zullinger quarry was filled with eastern bituminous coal fly ash from a Maryland power plant.

Consultant studies were completed on certain aspects of the Zullinger fly ash fill during the initial phases of site operation, in support of a State permit application (Berger and Potomac, 1973-75; Berger, 1973). The Zullinger quarry fly ash disposal site has also received mention in an unpublished report prepared for the Utility Solid Waste Activities Group and the Edison Electric Institute by the Envirosphere Company (1979).

^aSenior Hydrogeologist, Dunn Geoscience Corp., 3806 Market St., Camphill, Pennsylvania 17011. Received November 1981, accepted February 1982. Discussion open until November 1, 1982.



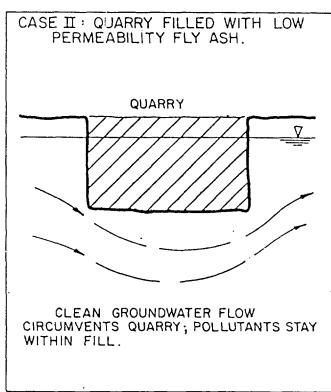


Fig. 5. Change in ground-water flow pattern.

For his specific model simulating the disposal of low permeability solid waste below the water table (unlined sites) in permeable aquifers (waste five times less permeable than the aquifer), Libicki concluded that: "when the permeability coefficient of the disposal is smaller from the one of aquifer, a flow round of the stream lines under the disposal will occur. This will effect decreased thickness of the pollutant stream leaving the disposal in relation to the depth of the disposal immersion." This situation is the best explanation for the unusual trend in ground-water quality monitoring data from the Zullinger fly ash disposal site.

It follows that the initial ground-water contamination that occurred at the Zullinger site could have been avoided if the quarry had been dewatered and the entire fly ash fill emplaced "in-the-dry." Higher fly ash densities and consequent lower permeabilities can be achieved with a properly compacted dry fill. The higher density would allow the disposal of more ash in a given volume; and the lower permeability would further minimize the possibility of long-term pollution. In addition, ground water would flow toward the site during dewatering, eliminating any potential for off-site ground-water pollution during the disposal operation. When the fill is completed, dewatering

would cease, and the water table would rebound. At this point, a low permeability fly ash plug would exist in the quarry. As previously discussed, ground-water flow would then tend to circumvent this low permeability plug.

An additional benefit offered by the disposal of acid fly ash in limestone quarries is the high alkalinity of limestone ground waters. The alkalinity of the limestone ground water at the Zullinger site probably buffered the acidity of the deposited fly ash. Background ground water had an average alkalinity of 168 mg/l. The most severely contaminated monitoring wells, #4 and #5, had average alkalinities of 70 mg/l and 73 mg/l. respectively. Had the fly ash been deposited in ground water with less natural alkalinity, the level of alkalinity in the contaminated zone may have been much lower. This is critical since alkalinity indirectly affects the solubility and mobility of metal ions in ground water. It is uncertain what effect, if any, the limited remedial liming of the fly ash had in stabilizing the decrease in alkalinity in downgradient ground water.

Some attenuation of pollutants by chemical processes probably occurred as ground water migrated away from the quarry. However, considering that ground-water flow was through fractured bedrock, the main attenuation processes

were probably physical dilution and dispersion. A thorough discussion of pollutant attenuation mechanisms in ground water is beyond the scope of this paper. However, the drastic improvement in ground-water quality at the Zullinger site clearly points to a physical mechanism that reduced the release of pollutants from the fill rather than to a process that increased the attenuation of released pollutants.

The ground-water quality monitoring data from the Zullinger fly ash fill is inadequate (due mainly to sampling technique and monitoring well construction) to determine if any trace elements migrated away from the fill. However, the alkaline environment afforded by the limestone ground water, and the natural isolation mechanism depicted in Figure 5 no doubt limited the mobility of trace elements in the fly ash.

ACKNOWLEDGMENTS

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Jeffrey R. Peffer attended the Pennsylvania State University where he obtained his B.Sc. in Geological Sciences in 1971, and a M.Eng. in Engineering Science in 1981. He is currently the Senior Hydrogeologist in the Camp Hill, Pennsylvania office of the consulting firm of Dunn Geoscience Corporation. From 1972 to 1979 he was a Regional Hydrogeologist with the Pennsylvania Department of Environmental Resources, He is a registered Professional Engineer in the State of Pennsylvania.

"FLY-ASH DISPOSAL"

Theis et al. (UNIVERSITY OF NOTRE DAME-ENGINEERING)

TABLE VI. Maximum increase of heavy metal over background concentration in soils (all concentrations $\mu g/g$).

Metal	Boring 13	Boring 21 (back- ground)	Me ₁₃ / Me ₂₁	Average Crustal Abundance (µg/g)	Source
As	6.5	3.83	1.7	1.8	18
Cd	0.66	0.30	2.20	0.2	19
Cr	17.0	12.8	1.33	100	18
Cu	13.4	15.4	0.87	40	19
Ni	14.9	17.6	0.85	80	20
Pb	20.7	9.50	2.18	13	18
Se	17.8	12.7	1.40	1	21
Zn	61.0	32.5	1.88	50	19

ally. These two oxides, however, are also major components of the surface of the fly ash. In view of the high solubilities of the metals under pond-water conditions, adsorption is the likely mechanism for the rapid attenuation of metal concentrations within the pond. The fact that this mechanism is unable to control the large pulses of metals which arise from operational variability suggests a more complex phenomenon may be occurring, in which kinetic factors may be important.

The extent of the accumulation of the trace metals in the soil around Pond 1 can be assessed through a comparison with background soil levels. Well 13 contained the maximum or near-maximum concentrations for each metal. Well 21 was located 500 m from the pond and is considered representative of background conditions. Table VI gives ratios of soluble metals in Well 13:background as well as average crustal abundances as reported in the literature. It is evident that accumulation of metals through precipitation and adsorption over background is occurring. If the increases shown are attributed to ash pond seepage, then this has taken place over a period of 2.5 years. It is not clear that the higher levels which exist are excessive in view of natural abundances, with the exceptions of arsenic and cadmium. The high selenium concentrations—even in the background samples—are as yet unexplained. Further increases in soil metals are possible. The problem becomes an interesting one to model.

The matter of metal concentrations which flow directly into the lake from the pond is one which must be addressed further. Analysis is difficult because the site layout leaves room for only one boring line between the ponds and the lake. At this time, it seems reasonable to assume metal attenuation pat-

terns on the lake side of the pond, similar to those observed and described previously for the opposite side. Metal concentrations attenuate rapidly; however, short-term perturbations may create momentary large concentrations entering the lake water.

SUMMARY

For the fly ash disposal site studied, it has been found that trace metals are released into the groundwater. In general, the concentrations are low, although they are sensitive to the ash loading rates and procedures. Rapid attenuation occurred for most metals very close to the pond itself. Many of the components of fly ash, especially iron and manganese oxides, are effective metal scavengers once they are formed in the pond. These oxides are, however, unable to dampen the curious peaks of metals which were observed and were related to the operation of the ponds and the power plant. This suggests that at sudden increases in ash concentrations there is either insufficient time or unfavorable local conditions (such as low pH) for the oxides to exert controls. If this is the case, simple pH adjustment, using lime or limestone, in the pond to a more alkaline range should control metal release. Lime could elevate the pH, causing precipitation of insoluble hydroxides of trace metals and promoting the formation of the sorbing hydrous oxides. Little excess sludge would be produced because of the low alkalinity of the pond water. Limestone would produce more sludge, but would also bring about the formation of insoluble metal carbonates prior to their release into the groundwater.

The behavior of trace metals, once released into the groundwater, is dependent upon the site hydrologic characteristics and the water quality differences between seepage water and natural groundwater. In this study, metals were found to accumulate in the soil due to precipitation and adsorption onto the hydrous iron and manganese oxides.

If the accumulations of metals in soils is deemed to be a problem or if the filterable concentrations of metals in the water are considered too high even after remedial pH adjustment in the pond (for example, nickel is naturally very soluble in this environment and the Ni²⁺ ion shows little tendency toward adsorbing onto local solid phases), then there may be no alternative except to limit the extent and quantity of pond seepage. Natural or chemical lining materials could be used for

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